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IN RALA PROCESSES

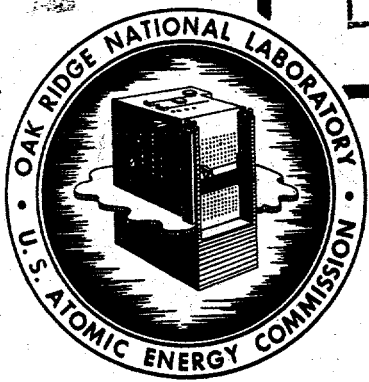
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No. 3 of 43 series A

CHEMICAL TECHNOLOGY DIVISION

## DESIGN CONSIDERATIONS IN RALA PROCESSES

[illegible]

Work by: G.B. Berry  
R.E. Blanco  
L. Brewer  
I.R. Higgins  
A.J. Humphreys  
R.H. Vaughan

NOV 8 1951

Operated by

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A circular black and white stamp. The outer ring contains numbers 1 through 12. The inner text reads: "RECEIVED" in large, bold, sans-serif capital letters. Below it, "NOV 9 1951" in a smaller font. Underneath that, "OFFICE OF" and "DIRECTOR" in two lines. At the bottom, "FEDERAL BUREAU OF INVESTIGATION" and "U. S. DEPARTMENT OF JUSTICE" in two lines. The stamp is slightly tilted.

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1.0 Abstract

An ion-exchange RaLa purification process appeared promising and a small cubicle was erected to demonstrate the process at kilocurie levels.

## 2.0 Introduction

Kilocurie quantities of Lanthanum 140 were required by the AEC in 1945. A process was developed and equipment installed in 706-D Building for the separation of barium 140, a fission product and the parent of lanthanum 140, from the nitric acid solution of irradiated uranium metal. Originally metal irradiated in the ORNL pile was used, but subsequent increased production demands required the use of Hanford-irradiated metal, shipped to Oak Ridge in specially designed lead carriers. The steadily increased production with attendant increases in radiation exposure hazards placed emphasis on improving the process efficiency and redesigning accessible equipment to minimize exposure hazards.

The entire process as installed in 1945 was reviewed and five general recommendations were made (RaLa Process Study Preliminary Report No. 1 by F.L. Culler et al, Central Files No. 49-4-38 dated 6 April 49). The advantage of one plan over another was dependent upon the ultimate capacity desired, the estimated required longevity of the plant, the period of down time for construction tolerable, and the relative urgency of making the recommended changes. After reviewing the available information, the AEC directed that a new permanent plant be erected at another installation, and that Oak Ridge make such changes as were required to alleviate the exposure hazards to personnel and insure the continued production of 2500 (later increased to 10000 curies) curie runs of satisfactory purity.

### 3.0 Purification Processes

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The barium product was separated from the dissolver solution by co-precipitation with lead as the sulphate. The sulphate was converted to the acid-soluble carbonate by metathesis with potassium carbonate solution. The carbonate was dissolved in nitric acid and the lead removed by electrolysis. The barium nitrate solution contained as contaminants, iron, chromium, nickel, cerium, silica, and strontium.

#### 3.1 Chemical Precipitation

The purification of the barium was accomplished by precipitating it from the nitrate solution with fuming nitric acid in which all but the barium and strontium were soluble. A second precipitation with hydrochloric-ether removed the strontium, leaving the product, barium chloride, as a soluble precipitate.

The precipitations were carried out in glassware in lead-shielded cubicles. The operations were visually followed with periscopes until successive runs (usually three maximum) had so darkened the glassware by exposure to the intense radiation that observation was impossible and the glass equipment would then have to be decontaminated and replaced. This was complicated by the fragility of the equipment, the confined working space, and the short working time permissible in the field of the residual radioactivity.

New cubicles were designed which featured remote instrumentation (making observation and therefore replacement of the equipment unnecessary) but final working drawings were held in abeyance pending the outcome of experiments with an ion-exchange process which seemed likely to supplant the chemical precipitation purification process described above.

#### 3.2 Ion Exchange

The value of resins for separating chemical elements has been known for sometime. A process was devised and reported in 1945 for the separation of barium from a solution of uranium slugs, however, the flow rates were so low that the barium losses by decay were disproportionally large and the process was not considered for plant production; however, a modification of the process for the purification of barium, after a rough separation from the uranium solution by chemical precipitation means, was entirely feasible. Briefly, the modified process consists of the absorption of the barium product on the resin, the selective elution of the undesired contaminants, and the final removal of the barium with nitric acid. The chelation agent, versene, ethylene diamine tetra acetic acid, has the effect of shifting equilibrium constants of many compounds depending upon its concentration and the pH of the solution. Use is made of this characteristic to make a total of some four possible modifications of the resin absorption process.

The first, the acetate process, requires that the sulfate precipitate from the precipitation step be metathesized and taken up in nitric acid solutions for absorption on the column, the contaminants then being selectively eluted with sodium citrate solutions of various pH's. The sodium is removed with hydrochloric acid and the barium product with nitric acid.

Purification Processes (continued)

A second modification uses versene to elute the contaminants, with a remarkable increase in reaction rate and a decrease in the quantity of solutions required.

A third variation consists of using versene to dissolve the sulphate precipitate, thereby obviating the need for metathesis which has always been a troublesome and unpredictable step. This variation, however, requires the use of two columns, the second being required to separate barium and strontium which behave quite similarly chemically; also, the pH is quite critical, necessitating pH-indicating instruments.

The fourth modification is a one-column process which is very similar to the versene two-column process except that not so clean a separation of barium and strontium is attained, and the barium product contains an appreciable quantity of strontium. The selection of the design process depended to some extent upon the specifications imposed by Los Alamos on the product received by them, and on the relative degree of aversion to the metathesis step. Unit Operation and Laboratory investigations of the acetate citrate process indicated less than 1% barium losses and this process was selected for a demonstration. See Sketch A.

A test cubicle was designed for erection in the 706-D Building to test the ability of resin to function at high activity levels. Radiation is known to dissociate water with the formation of hydrogen peroxide and the evolution of hydrogen gas. Resin columns are peculiarly sensitive to "vapor locking". Whether or not gas evolved during processing of the barium at high levels of radiation would effect the operation of the column could be determined only by observing such a column in operation at full scale.

#### 4.0 Description of Test Cubicle

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##### 4.1 General

The ion exchange equipment, consisting of a gravity feed tank, ion exchange column, waste and product tanks, samplers and a column-effluent radiation monitor, was designed to be shop-fabricated in a simple angle-iron frame work unit. The entire equipment was then transported and set-up as a unit, connected to pipe lines running to existing facilities (for feed, off-gas and waste disposal), and shielded with a lead-brick wall, one foot thick (see sketches B & C).

The angle-iron framework was 20 inches square and six feet high. It was set on the floor of 706-D Building nine inches from the concrete shielding wall of A-cell, and process pipe connections were made through convenient A-cell wall-ports. The lead brick wall was then erected to shield the three open sides and top.

All cubicle tanks were connected by their off-gas lines to the waste tank, which was connected to A-16 vessel off-gas system. Several A-cell wall-ports were left unplugged so that the cubicle was ventilated by the A-cell ventilation system.

Continuous observation of the glass column was provided by a Kollsman-type periscope mounted on the face of the cubicle.

The process tanks and piping were of 347 stainless construction.

The vertical column was constructed of pyrex glass, joined to the piping with special fittings machined from fluorothene. The ion exchange resin was charged to the column as a slurry, finally resting on sand and glass beads supported by 100-mesh platinum screen in the lower fluorothene fitting. The resin was discharged by back washing it from the column to the hot waste drain system. The column was surmounted by a deaerator, essentially an enlargement in the vertical section of the resin disposal line that would permit expansion of the resin by a gentle backflow. The backflow might be necessary to give any gases evolved or adsorbed on the resin (that would otherwise cause "vapor locking" or channeling in the resin bed) an opportunity to escape.

The gravity flow from the feed tank was adjusted with a needle globe valve. The effluent from the column was conducted by a Saran tube through a shielded ion chamber and thence to a multi-port plug valve for diversion to either the waste or product tank.

The ion chamber monitored the relative radioactivity of the column effluent, producing traces on a recorder that were characteristic of the ions being removed from the column; thus affording a valuable process control.

Description of Test Cubicle - continued

Three samplers were provided, for the feed, waste and product solutions. The sampler was of a unique design (developed by the Unit Operations Section) that featured a sample of discrete volume that could be withdrawn into a shielded carrier. The sampler consisted of a 4-port plug valve, the plug having a single, straight-through passage. The suction of a CL-5 air jet drew solution from the tank to be sampled, through the horizontal ports of the plug to the jet and thence back to the tank. Turning the plug to the vertical position permitted the liquid trapped in the plug passage to fall into a sample receptacle, which in turn could be withdrawn into a lead-shielded carrier. The sampler was fabricated as a unit, lead-shielded, so that it could be supported by and become a part of the shielding wall (see sketch D).

The samplers were designed so that the sample valves could be washed, the wash flowing by gravity through a drain line leading to the waste tank. During a decontamination procedure, the waste tank was inadvertently overflowed and the decontaminating chemicals, uncomfortably "hot", flowed from the sampler channel. The spill could have been hazardous, had it occurred during a run.

4.2 Operation

The cubicle operated satisfactorily, in general. Some 3000 curies were processed: The shielding was adequate, the equipment functioned as planned, and the effects of high levels of radiation upon the ion exchange column were observed.

One sampler (feed tank) failed to function. After dismantling, it was found that the teflon liner of the sampler valve was undersize and the resulting annular gap between the liner and the valve body vented the jet suction line, so that liquid could not be drawn from the tank.

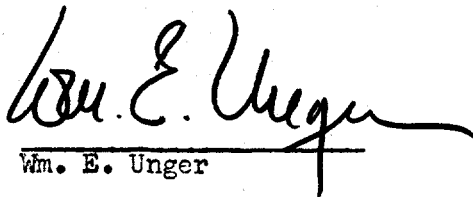
The column developed a high pressure drop which interfered with the feed and eluting steps. A platinum screen designated for the eluate line, to prevent the lodging of ion exchange resin in the eluate line during resin dumping, was, by mistake, installed in the feed line from the feed tank. The feed, known to contain suspended matter of uncertain origin, apparently progressively plugged the screen. The feed solution also contained appreciable quantities of silicates which are believed to have been the cause of a flocculent layer of material 1/4 inch thick that formed on the surface of the ion exchange resin and contributed to the pressure drop across the system. A feed pressure of six pounds per square inch was not sufficient to maintain satisfactory feed rates throughout the run.

A leak developed in the Corning flange junction between the column and a fluorothene adapter. It is probable that the fluorothene plastic relaxed slightly, perhaps from the effects of radiation, relieving the sealing pressure on the joint; A hand hole was cut through the shielding wall and the flanges tightened after the first run. The column did not leak again.

5.0 Recommended Design Considerations

Economy dictates the maximum use of present equipment. The existing dissolver, precipitator, and waste tanks can be used without major changes. New purification equipment can be separately shielded and process connections to existing equipment made through shielded lines. The versatile ion-exchange purification process is apparently superior and its selection is recommended.

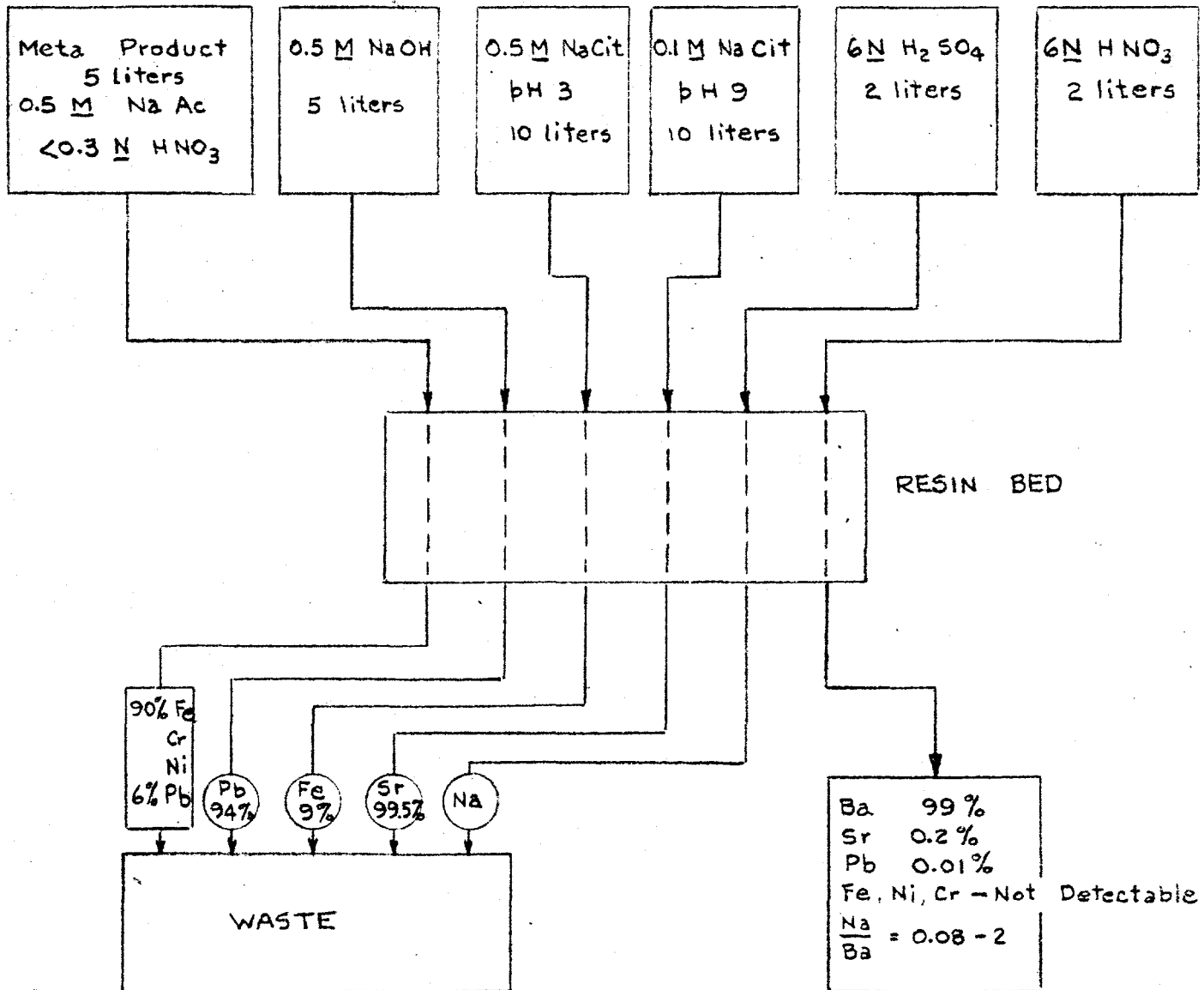
The final purification equipment should be compactly arranged in a framework of simple geometric shape which can be housed in floor pits, making use of the earth for shielding. The pits should be so arranged that overflows drain by gravity to hot waste storage to eliminate the hazard of spills.

  
Wm. E. Unger

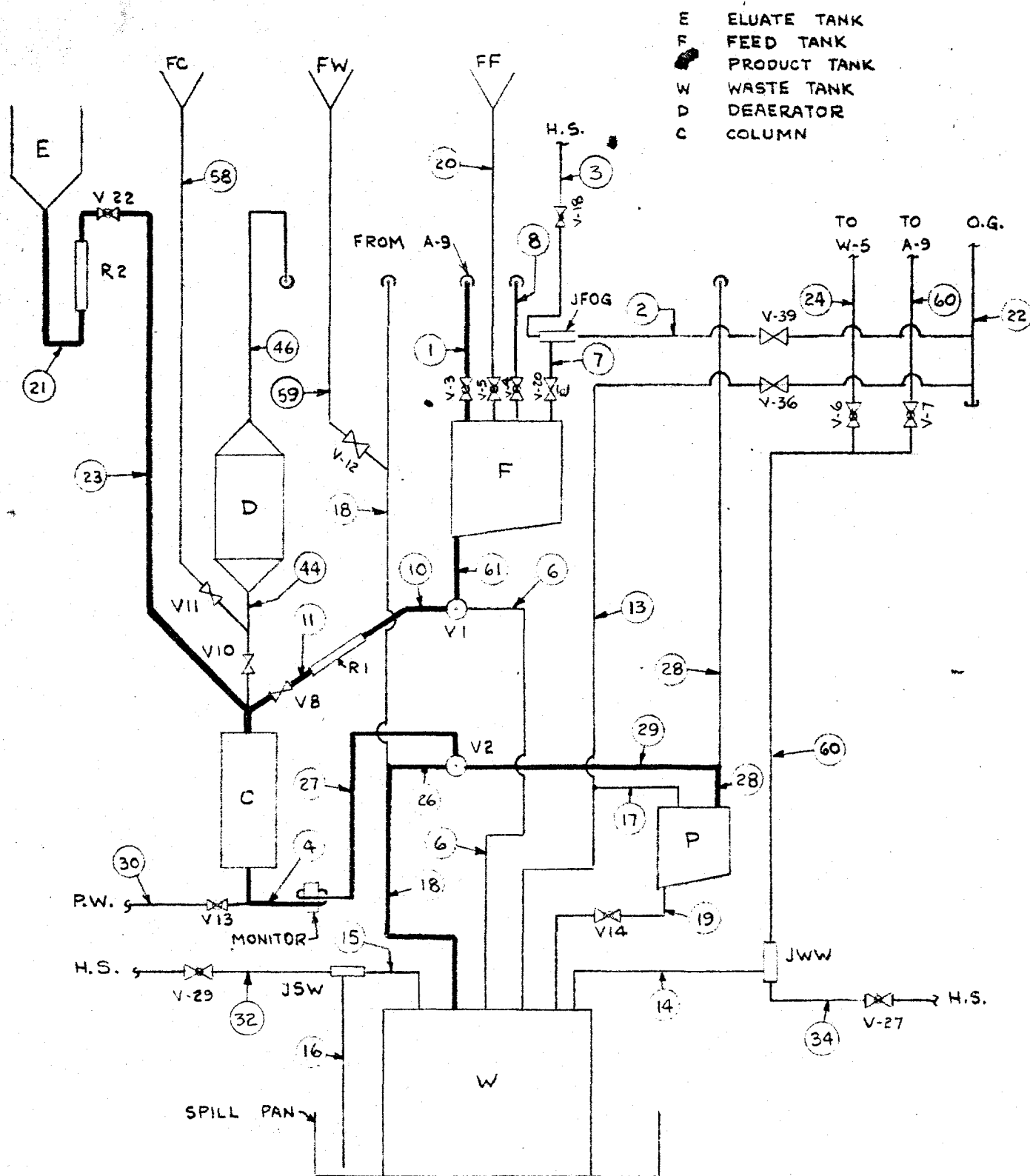
6.0 Bibliography

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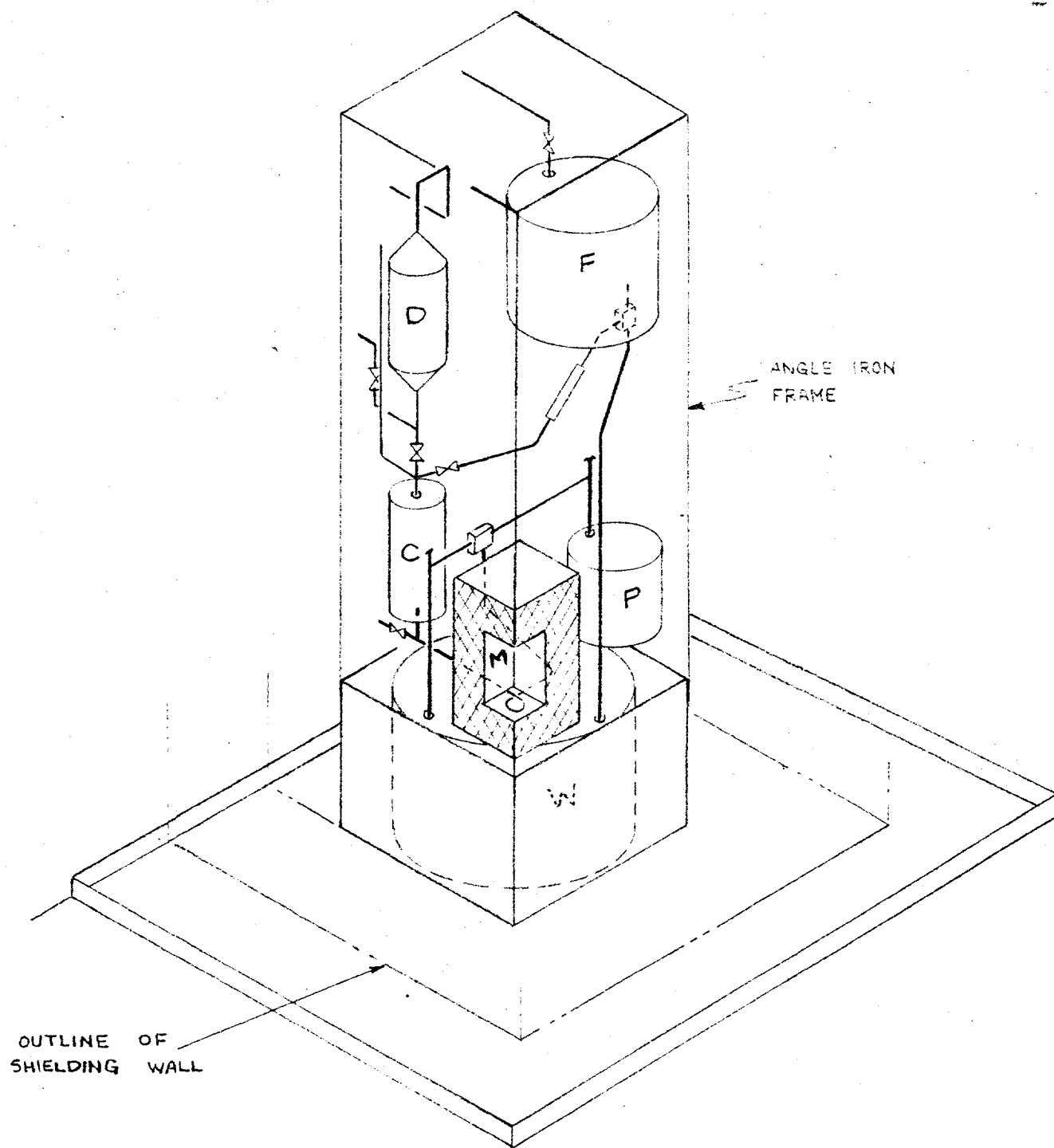
- (1) Culler, F.L., Goeller, G.E., Unger, Wm.E., RaLa Study Preliminary Report #1, ORNL Central Files 49-4-38
- (2) Higgins, I.R., Semi-Works Demonstration of a Precipitation and Ion Exchange Process, ORNL-621
- (3) Higgins, I.R., Blanco, R.E., Unger, Wm.E., Preliminary Demonstration of RaLa Ion Exchange Processes at the Kilocurie Level, ORNL-623
- (4) Boyd, G.E., Cohn, W.E., Davies, T.H., Schubert, J., et al The Extraction and Decontamination of Ba  $^{140}$  from Uranyl Nitrate Solutions by an Absorption Process, CN-2563
- (5) Baldwin and Savolainen, Laboratory Development of the RaLa Process MON-330, 12 June 1947.
- (6) Eister, W.K., Semi-Works Development of the RaLa Process, ORNL-231.



SKETCH "A"

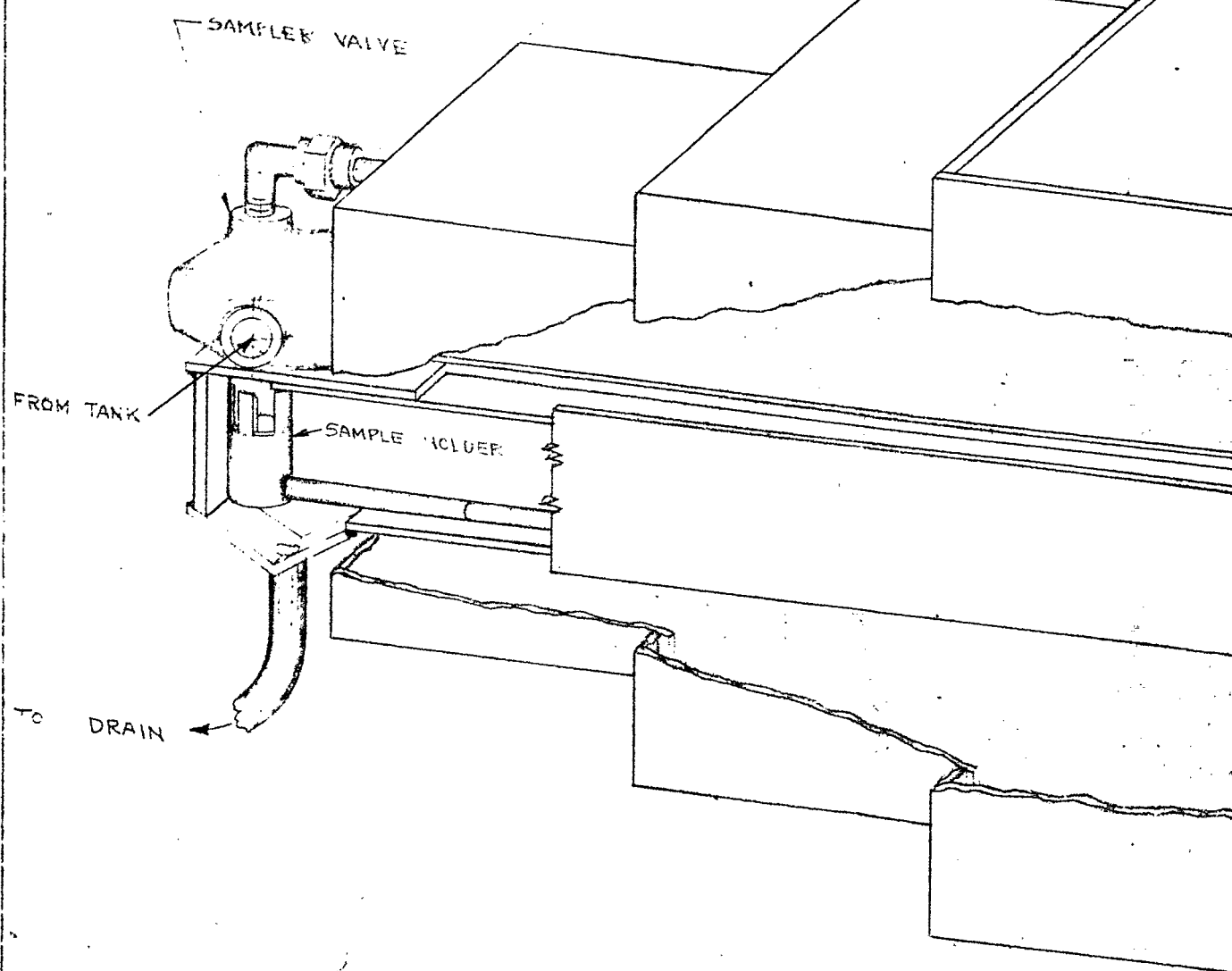


RESIN PURIFICATION  
 SCHEMATIC EQUIPMENT FLOW SHEET  
 SKETCH "B"

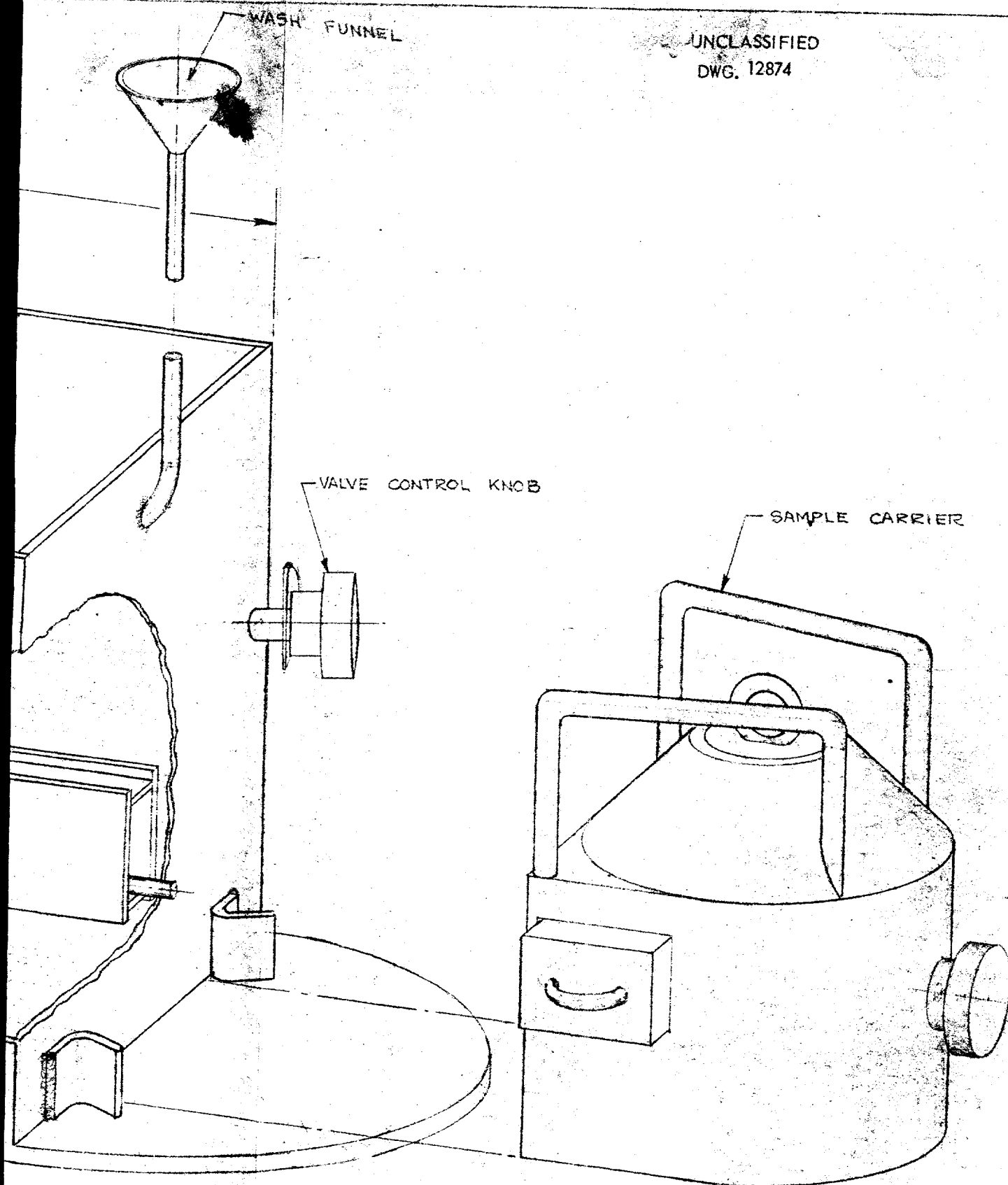


SKETCH "C"

12



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SKETCH D

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GBB. 2-12-5

## DRAWING SCHEDULE

## RALA RESIN PURIFICATION

TD-1277 to TD-1284 inclusive	Teflon 3-way 1/4" Plug Valve
TD-1291	Feed Tank - Detail
TD-1292	Waste Tank - Detail
TD-1293	Deaerator - Detail
TD-1294	Thermo - Flowrator Dimensions
TD-1305	Column
TD-1306	Product Tank - Detail
TD-1307	Schematic Flowsheet
TD-1308	Piping Inside Cell
TD-1309	Cell Structure - Assembly and Details
TD-1311	Panelboard Layout
TD-1319	Piping Outside Cell - Arrangement and Details
TD-1320	Schematic Sampler Arrangement
TD-1328	Schematic Arrangement Manometer Piping
TD-1335	Special Fittings
TD-1336	Periscope Support
TD-1338	Valve Extension Handles
TD-1340	Column - Assembly and Details
TD-1341	Eluate Tank
TD-1390	Eluate Tank Shield and Spill Pan
TD-1392	Schematic Arrangement Manometer Piping
TD-1398	Sample Tube
TD-1440	Additional Shielding
E-6321	Sampler - Assembly
E-6322	Sampler - Detail
D-6323	Details of Sample Carrier
D-6324	Miscellaneous Details
D-6325	Valve Detail
C-6338	Detail of Receiver Frame
D-6348	Tongs Detail
B-6517	Shielding Support

